



Comparative study of imazalil degradation in three systems: UV/TiO₂, UV/K₂S₂O₈ and UV/TiO₂/K₂S₂O₈

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ABSTRACT

The degradation of imazalil was achieved in three different advanced oxidation processes, namely UV/TiO₂, UV/K₂S₂O₈ and UV/TiO₂/K₂S₂O₈. The most relevant findings showed that for the UV/TiO₂ system, the best efficiency was obtained at alkaline pH for which the rate of degradation is governed by imazalil adsorption onto TiO₂, while for the UV/TiO₂/K₂S₂O₈ system, the best efficiency was obtained at acidic pH for which the rate of degradation is governed by persulfate adsorption onto TiO₂ surface. In this last case, sulfate adsorption can reduce e⁻/h⁺ recombination while sulfate radicals are generated. Concerning the UV/K₂S₂O₈ system, it was shown that pH does not play an important role in the degradation and persulfate concentration is the main factor governing the rate of degradation.

Experiments with *tert*-butanol were achieved at different pH and the results showed that at pH = 6.5 and with a ratio [K₂S₂O₈]/[imazalil] = 100, hydroxyl radicals were responsible for 67.6% of the degradation in the UV/TiO₂ system, 3.1% in the UV/K₂S₂O₈ system, meaning that the degradation should be mainly attributed to sulfate radicals and 33.2% in the UV/TiO₂/K₂S₂O₈ system meaning that both OH• and SO₄•⁻ were involved in the degradation.

Coming to the comparison of photoproducts by using LC/MS/MS (pH = 6.5), the conclusion is that hydroxylated products were more produced in the UV/TiO₂ system while a mechanism involving a charge transfer would be responsible of the degradation with persulfate systems. TOC analysis shows that total mineralization was reached faster in systems containing persulfate.

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1. Introduction

Water in rivers and rain drops contain a large number of organic and inorganic impurities which can be degraded using advanced oxidation processes (AOPs). These processes are based mostly on the generation of hydroxyl radicals which are highly reactive and nonselective oxidants toward organic compounds. As broadly accepted, photogenerated valence holes are formed when TiO₂ particles are irradiated by UV light, which leads to oxidation of

OH⁻ or H₂O by holes resulting in hydroxyl radicals that are capable of destroying most organic species [1]. Oxygen is necessary in these systems; it acts efficiently as an electron trap, preventing the recombination of photogenerated electrons and holes. When oxygen is limited, the rapid recombination of electrons and holes in TiO₂ would markedly reduce its photocatalytic actions [2]. Instead of oxygen, inorganic oxidants such as IO₄⁻, S₂O₈²⁻, BrO₃⁻, ClO₃⁻ and H₂O₂ can be used [3–7]. These oxidants improve the performance of UV/TiO₂ by reducing the probability of recombination of the photogenerated electrons and holes, thus availing more holes for oxidative degradation of organic contaminants and by forming other reactive radicals (SO₄•⁻, BrO•, BrO₂•, IO₃•).

Furthermore, it has been claimed by several authors that the degradation using the UV/oxidants systems could be more efficient than the UV/TiO₂ system [8–10]. In the UV/oxidants system, a great amount of reactive radicals (SO₄•⁻, BrO•, BrO₂•, IO₃•, etc.) other than OH• are produced which could be responsible of the organic compounds degradation. So it would be interesting to do the comparison between the three following systems UV/TiO₂,

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UV/oxidant and UV/TiO₂/oxidant to assess their respective performance.

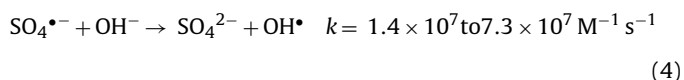
In this work, persulfate an inorganic oxidant was chosen for several reasons: It is a strong oxidant ($E^\circ(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{\bullet-}) = 2.01 \text{ V}$) [11] and its activation leads to the formation of the sulfate radical ($\text{SO}_4^{\bullet-}$) under a broad range of pH ($1 \leq \text{pH} \leq 10.5$) [12] which is an oxidant even stronger ($E^\circ(\text{SO}_4^{\bullet-}/\text{SO}_4^{2-}) = 2.6 \text{ V}$). Unlike hydroxyl radical, $\text{SO}_4^{\bullet-}$ is more selective [13] and it can react with molecules by three different mechanisms: (i) hydrogen abstraction, (ii) addition on double bond and (iii) electron transfer. This latter mechanism is not feasible by OH^\bullet with uncharged species which make sulfate radicals more advantageous when this mechanism is possible. Also, persulfate generates sulfate anions as end-product, which are practically inert and not considered as pollutants [8,14,15]. The persulfate amount required for the degradation is less than the one for other oxidants (i.e. peroxomonosulfate needs a high concentration to be used efficiently) [16] and it is an inexpensive oxidant.

Moreover, its presence can increase the kinetic of the mineralization of pollutants which is very important in the depollution of water [16–18] and a very good efficiency was obtained in all the cases where it had been tested [2,16,19–21].

In the UV/TiO₂/K₂S₂O₈ system, persulfate could be activated by electron transfer, heating and photolysis according to Eqs. (1)–(3), while in the UV/K₂S₂O₈ system, the activation is mainly attributed to the photolysis activation Eq. (2) [13,22].



On the other hand, pH could play a very important role in the repartition of dominant radicals involved in the degradation especially in the UV/TiO₂/K₂S₂O₈ system. For example, Liang and Su [23], studied the inter-conversion from sulfate radical to hydroxyl radical by the following reaction Eq. (4):



And they observed that:

At pH < 7, $\text{SO}_4^{\bullet-}$ is the predominant radical.

At pH = 9, both OH^\bullet and $\text{SO}_4^{\bullet-}$ are present.

At pH > 9, OH^\bullet is the predominant radical.

So it would be interesting to investigate the dominant radicals involved in each degradation system by using radical scavengers at different pH. Alcohols are usually used as hydroxyl radical scavengers, but since they can also scavenge sulfate radicals [24] the choice of the alcohol will depend of its kinetic rate constants toward the two radicals. In our study, *tert*-butanol (TBA) was used since its k_{OH^\bullet} is ca. $>1000 \text{ k SO}_4^{\bullet-}$ ($k_{\text{OH}^\bullet/\text{TBA}} = 3.8\text{--}7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{SO}_4^{\bullet-}/\text{TBA}} = 4\text{--}9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [25] meaning that at low concentration of sulfate, it is supposed to scavenge mainly hydroxyl radicals.

To accomplish this study, imazalil which is a fungicide belonging to the imidazole family was chosen, since its degradation using the UV/TiO₂ system was studied in a previous work and nine of its photoproducts were identified [26]. By using specific scavengers (alcohols, KI), it has been found that some of these photoproducts come from a hydroxylation while others were attributed to an electron transfer mechanism. On the other hand, the optimization of imazalil degradation using an experimental design was investigated using the UV/TiO₂/K₂S₂O₈ system [27].

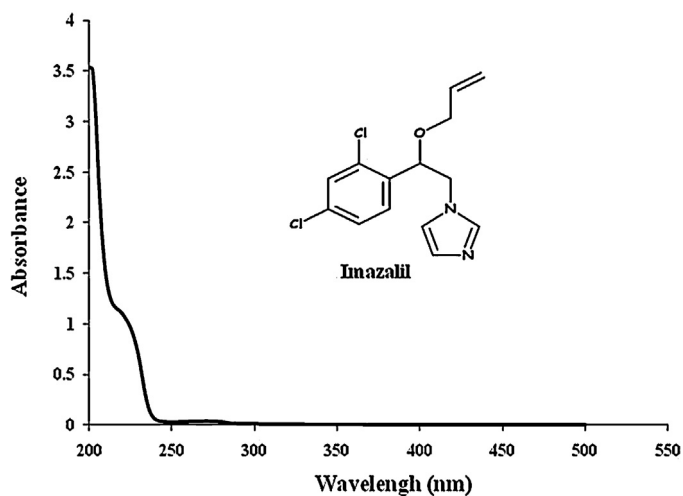


Fig. 1. Structure of imazalil and its UV-vis spectra.

The aim of this paper was (i) to study a new system of degradation for imazalil: UV/K₂S₂O₈, (ii) to compare it with UV/TiO₂ and UV/TiO₂/K₂S₂O₈ systems at different pH values and at different persulfate concentrations, (iii) to perform experiments with *tert*-butanol to find out the dominant radicals involved in each system (iv) to compare the photoproducts identified by LC/MS/MS in the three systems and (v) to follow the mineralization of imazalil by TOC analysis also in the three systems.

2. Materials and methods

2.1. Chemicals

Imazalil (Fig. 1), (*RS*)-1-[2-(allyloxy)-2-(2,4-dichlorophenyl)ethyl]-1H-imidazole (99% purity) was purchased from Sigma-Aldrich and used as received. Titanium dioxide Degussa P25 was provided by Degussa (Frankfurt, Germany) with a specific BET area of $50 \text{ m}^2 \text{ g}^{-1}$ and a mean particle size of 30 nm. Polyvinylidene fluoride PVDF filters ($0.45 \mu\text{m}$) were purchased from Millipore. Acetonitrile (quality HPLC grade and LC/MS/MS grade), potassium persulfate (K₂S₂O₈), and *tert*-butanol were purchased from Aldrich. Water was obtained from a Millipore Waters Milli-Q water purification system. Other reagents were at least of analytical grade.

2.2. Photoreactor and light source

The irradiation was carried out in an open borosilicate (Pyrex) glass cell (cut-off at 295 nm, 4 cm diameter, 9 cm height) equipped with a magnetic stirring bar and water circulating jacket. The light source was a HPK 125W Philips mercury lamp with main emission wavelengths at 365 nm and in a lesser extent at 312 nm, cooled with a water circulation. The radiant flux entering the irradiation cell was measured by a VLX-3W radiometer with a CX-365 detector (UV-A) and a value of 31 mW cm^{-2} was found. For all experiences, before and during irradiation, the suspensions were magnetically stirred.

2.3. Photocatalytic degradation procedure

Solutions of imazalil (25 mg L^{-1} equivalent to $84.4 \mu\text{mol L}^{-1}$) were prepared using Millipore Milli-Q deionized water and stored at 4°C in the dark. The pH values (3, 6.5, or 10) were adjusted by adding concentrated aqueous solutions of H₃PO₄ or NaOH to the desired value throughout the experiments. A magnetic stirrer was

used to induce satisfactory mixing of the solution in the reactor. A volume of 25 mL of aqueous imazalil solution was introduced into the reactor in all the experiments, the required amount of TiO_2 powder was (2.5 g L^{-1}) in the UV/ TiO_2 and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$ systems while no TiO_2 was added in the UV/ $\text{K}_2\text{S}_2\text{O}_8$ system. Different $[\text{K}_2\text{S}_2\text{O}_8]/[\text{imazalil}]$ ratios were used, 100, 250 and 500 equivalents to 8.4, 21.1 and 42.2 mM of persulfate. Before irradiation, in the experiments with TiO_2 , the suspension was stirred in the dark for 30 min to reach adsorption–desorption equilibrium, while in the UV/ $\text{K}_2\text{S}_2\text{O}_8$ system, the solution was stirred for 5 min before the irradiation to be sure to have a homogeneous solution. For degradation experiments, during the irradiation, aliquots suspension were sampled at regular time intervals and filtered through 0.45 mm PVDF syringe filters to remove TiO_2 particles immediately before analysis. In addition, aliquots from the UV/ $\text{K}_2\text{S}_2\text{O}_8$ system were also filtered to be in the same conditions for all the analysis. Total volume of the sample withdrawn was less than 10% (by volume) of the solution (i.e. 2.5 mL). Same procedure was performed in the presence of *tert*-butanol, which was added from the beginning of the experiences in the three systems.

2.4. Chemical analysis

2.4.1. HPLC/DAD

The kinetic profile of imazalil degradation during irradiation was monitored using Shimadzu VP series HPLC system consisting of LC-10AT binary pump, a SPD-M10A DAD and Shimadzu Class-VP software version (5.0). A $20 \mu\text{L}$ of filtered irradiated samples (25 mg L^{-1}) was directly injected. Analytical separation was performed using a column KROMASIL C4 ($250 \text{ mm} \times 4.6 \text{ mm}$, particle size $5 \mu\text{m}$) mobile phase, 70:30 (v/v) acetonitrile/water, a flow rate of 1 mL min^{-1} and the detection wavelength of 202 nm.

2.4.2. LC/MS/MS

The separation, evolution and identification of intermediates formed during the photocatalytic degradation of imazalil solutions were performed by using LC–MS/MS analysis with a system comprising an HP 1100 series HPLC comprising binary pump and autosampler (Agilent Technologies, Waldbronn, Germany) coupled to a API4000 Q trap mass spectrometer (Applied Biosystems/MDS Analytical Technologies, Foster City, CA, USA) and equipped with a Turbo IonSpray source. Instrument control, data acquisition and processing were performed using the associated Analyst 1.5.1 software. The LC separation of the $20 \mu\text{L}$ injected sample was carried out on a Symmetry C₁₈ column ($100 \text{ mm} \times 2.1 \text{ mm}$, particle size $3.5 \mu\text{m}$) from Waters (Milford, MA, USA). Elution was performed at a flow rate of 0.3 mL min^{-1} with water containing 0.1% (v/v) formic acid as eluent A and acetonitrile containing 0.1% (v/v) formic acid as eluent B, employing a linear gradient from 95% A to 60% A in 30 min. Then, column re-equilibration was performed for 10 min.

The injection duty cycle was 40 min, taking into account the column equilibration time. The mass spectrometer was initially tuned and calibrated using polypropylene glycol, reserpine and Agilent Tuning Mix (all Applied Biosystems, Foster City, CA, USA) according to the manufacturer's instructions. Q1 and Q3 were adjusted to $0.7 \pm 0.1 \text{ a.m.u. FWHM}$ (Full Width at Half Maximum) for Full Scan, Product Ion Scan and Single Ion Monitoring mode, referred to as unit resolution. MS analysis was carried out in positive ionization mode using an ion spray voltage of 5500 V. The nebulizer (air) and the curtain gas flows (nitrogen) were set at 30 and 50 respectively. The Ion Spray source was operated at 450°C with the auxiliary gas flow (air) set at 10.

First full scan in positive and negative mode (m/z range 50–500, scan time, declustering potential $\pm 30 \text{ V}$) was performed in order to identify the intermediates. Then, product ion scan MS/MS mode (declustering potential $\pm 30 \text{ V}$, collision energy 20 eV, precursor ion

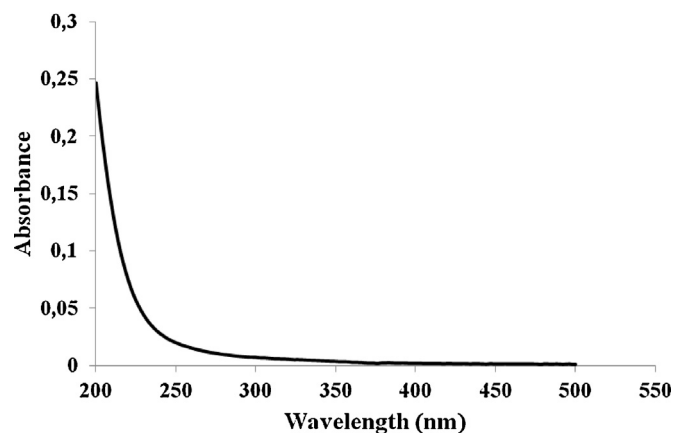


Fig. 2. Absorption spectra of potassium persulfate ($1.85 \times 10^{-4} \text{ M}$) in water solution.

m/z : 297, 255 and 159) was used for structure elucidation of the main degradation product. As positive ionization mode gave best sensitivity, this polarity ionization mode was retained for reaction kinetic photodegradation determination in single ion monitoring (SIM) (declustering potential 30 V). The ions selected for performing SIM, were 246, 257, 273, 313, 329 and 331.

For the HPLC–MS/MS kinetic studies of imazalil and its products of degradation, aliquots of the reaction mixture were taken at the beginning of the experiment and at regular time intervals during irradiation and after filtration to separate the TiO_2 particles.

2.4.3. Total organic carbon analysis

In order to determine the extent of mineralization, total organic carbon (TOC) measurements were performed on filtered suspensions samples using TOCv-TN analyzer Shimadzu equipped with a Shimadzu ASI-V auto sampler device. 1 mL sample was mixed with 5% HCl solution (2 N) by purging out air for 90 s. Each sample was measured twice and a final TOC value was determined by calculating the average over the two measurements. Calibration was achieved by injecting standards of succinic acid solution.

2.4.4. UV/vis spectrophotometer

The spectra of imazalil and potassium persulfate were performed between 200 and 500 nm in an aqueous solution using a Lambda 950 UV-Vis spectrophotometer (Perkin Elmer). Two quartz cuvettes whose optical path length is 1.0 cm were used.

3. Results and discussion

3.1. Absorption spectra of anion persulfate

Studies in the literature showed that persulfate could be activated between 193 and 351 nm [28]. Fig. 2 shows the absorption spectrum of the persulfate at 0.1 M. It can be concluded from this figure that the main wavelength emitted from HPK lamp which is 365 nm is not able to activate persulfate. On the other hand, the one at 312 nm, even if its intensity is low, could activate persulfate anions due to its high quantum yield ($\Phi = 1.1$) [29].

3.2. Preliminary experiments

Preliminary experiments were performed to determine the extent of imazalil (25 mg L^{-1}) adsorption onto TiO_2 as well as its photostability under different pH. From these preliminary experiments it was found that the adsorption of imazalil onto TiO_2 varied with pH. For acidic pH, the adsorption was insignificant (1%) since the surface of TiO_2 ($\text{pH} < \text{pH}_{\text{pzc}}$) and imazalil ($\text{pK}_a = 6.52$) were both

Table 1

Constant rate of imazalil in the different systems containing persulfate [imazalil] = 25 mg L⁻¹, [TiO₂] = 2.5 g L⁻¹.

Experiment conditions ([K ₂ S ₂ O ₈] – pH)	<i>k</i> (min ⁻¹) (UV/K ₂ S ₂ O ₈)	<i>k</i> (min ⁻¹) (UV/TiO ₂ /K ₂ S ₂ O ₈)
8.4 × 10 ⁻³ M – pH 3	0.150	0.466
8.4 × 10 ⁻³ M – pH 6.5	0.151	0.278
8.4 × 10 ⁻³ M – pH 10	0.150	0.127
2.11 × 10 ⁻² M – pH 3	0.368	0.504
2.11 × 10 ⁻² M – pH 6.5	0.374	0.367
2.11 × 10 ⁻² M – pH 10	0.356	0.195
4.22 × 10 ⁻² M – pH 3	0.536	0.498
4.22 × 10 ⁻² M – pH 6.5	0.596	0.401
4.22 × 10 ⁻² M – pH 10	0.572	0.361

positively charged and electrostatic repulsion between them can occur. For neutral and alkaline pH, the adsorption was about 5% and 9% respectively. Concerning the photostability, the photodegradation of imazalil did not exceed 3% whatever the pH.

Additional imazalil degradation experiments performed in the dark for 30 min using different ratio [persulfate]/[imazalil] = 100, 250 and 500 and different pH values were carried out. The results show that even in dark, persulfate can oxidize imazalil for the different pH tested, since 7% of imazalil were degraded for [persulfate]/[imazalil] = 100. In addition, it is shown that an increase of the [K₂S₂O₈]/[imazalil] ratio lead to a slight increase in imazalil degradation since 8.5% and 14.5% of degradation were obtained respectively for [persulfate]/[imazalil] = 250 and 500 for the pH tested. This degradation could be explained by the thermal activation of persulfate which lead to the formation of sulfate radicals (Eq. (3)).

In this context a control of the temperature would be very essential in the following experiments using persulfate.

3.3. Comparison of imazalil degradation in the systems UV/TiO₂, UV/K₂S₂O₈ and UV/TiO₂/K₂S₂O₈ at different pH and different persulfate concentration

Experiments with imazalil, in the three different systems were carried out at three different pH (3, 6.5, 10) and three different persulfate concentrations (8.4, 21.1, 42.2 mM). Table 1 shows only the values of the rate constant *k*_{app} obtained in the two systems containing persulfate anions, since results obtained with UV/TiO₂ were already presented in Ref. [26]. In all the experiments, we assume that a pseudo first order rate for the degradation of imazalil is obtained and *k* values were obtained from the graph ln(C₀/C) = *kt* (R² > 0.99).

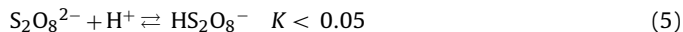
3.3.1. Influence of pH

It has been found for the UV/TiO₂ system, that the lowest degradation rate of imazalil (25 mg L⁻¹) was obtained at acidic pH (*k* = 0.07 min⁻¹) and the highest at alkaline pH (*k* = 0.13 min⁻¹) while for pH = 6.5, *k* = 0.11 min⁻¹. This difference was explained by the adsorption of imazalil (p*K*_a = 6.5) onto TiO₂ surface which is pH dependent [30]. At high pH values, degradation of imazalil is faster mainly due to a higher rate of imazalil adsorbed according to the Langmuir–Hinshelwood model.

From Table 1 we observe that whatever the experimental conditions, the presence of K₂S₂O₈ in the solution gives a more efficient degradation than in the UV/TiO₂ system which demonstrates the efficiency of sulfate radicals for imazalil degradation but we should not forget that the quantity of persulfate is very high so the SO₄•⁻ are in excess.

In addition, Table 1 shows that for a given persulfate concentration in the UV/TiO₂/K₂S₂O₈ system, the fastest imazalil removal was obtained at pH = 3 and the slowest at pH = 10. These results can be explained by the fact that at acidic pH, S₂O₈²⁻ and

HS₂O₈⁻ (Eq. (5)) are easily adsorbed onto the positively charged TiO₂ surface (pH_{pzc} = 6.3 for TiO₂) and hence, electron photogenerated in the conduction band can easily react with persulfate according to Eq. (1) to give the reactive SO₄•⁻ species.



The more the pH increases, the less the adsorption onto TiO₂ occurs (TiO₂ surface becomes more negatively charged) explaining the lowest efficiency of the system at pH = 10.

From Table 1, we can also see that for the UV/K₂S₂O₈ system, for a given imazalil concentration, all the rate constants (*k*) were almost identical whatever the pH, meaning that the pH does not play an important role in this case. Lin et al. [31] obtained the same conclusion for phenol degradation.

3.3.2. Influence of persulfate concentration

Table 1 shows that at pH = 3 and for the two lowest concentrations, the UV/TiO₂/K₂S₂O₈ system is more efficient than the UV/K₂S₂O₈ system, but a reversed result is obtained for the highest concentration. This finding could be explained mainly by an adsorption effect. For the lowest concentration, persulfate adsorption onto TiO₂ depends on the persulfate concentration according to Langmuir adsorption model and the amount of sulfate radicals will be proportional to the surface coverage by persulfate. However for the highest concentration, the surface is totally covered and an increase of persulfate concentration can no longer produce further sulfate radicals by this mechanism. A saturation effect occurs explaining why the rate constant values obtained for UV/TiO₂/K₂S₂O₈ system remains almost constant while a higher rate constant was found for UV/K₂S₂O₈ system. In this last case more sulfate radicals can be generated both by photolysis and thermal activation and enhance the rate of degradation. Different results are obtained at pH = 6.5 and 10 since persulfate adsorption is reduced and the saturation is not reached. In the two systems, the addition of persulfate leads to an increase of the rate of degradation, since more sulfate radicals can be generated. Concerning the UV/TiO₂/K₂S₂O₈ system it is assumed that the mechanism of degradation evolves in function of pH. At acidic pH, the degradation will be mainly controlled by the adsorption of persulfate which will yield sulfate radicals, whereas at alkaline pH, the degradation will be mainly governed by imazalil adsorption and hydroxyl radicals (UV/TiO₂ system). For example, at pH = 10 for the lowest concentration of persulfate, nearly the same rate constant is obtained for UV/TiO₂/K₂S₂O₈ and UV/TiO₂ systems. In this case, as the K₂S₂O₈ concentration is low we can assume that the mechanism of the degradation is mainly governed by UV/TiO₂ which is more efficient at pH = 10. At intermediary pH, both mechanisms can occur but their respective influence will depend on pH and persulfate concentration.

3.4. Effect of *tert*-butanol on the degradation of imazalil

In order to better understand which radicals (hydroxyl or sulfate radicals) are involved during the degradation, alcohols (hydroxyl radical scavengers) have been used such as *tert*-butanol, ethanol, methanol [2,21,24]. In this study, experiments using *tert*-butanol (TBA) were performed in the three systems at different pH. This latter is a scavenger for both hydroxyl and sulfate radicals but with different kinetic rate constants: *k*_{TBA-OH•} = 6 × 10⁸ M⁻¹ s⁻¹ and *k*_{TBA-SO₄•⁻} = 8 × 10⁵ M⁻¹ s⁻¹ (*k*_{TBA-OH•} is ca. > 1000*k*_{TBA-SO₄•⁻}) [25]. From our previous work in which methanol and isopropanol were used as hydroxyl scavengers during the photocatalytic degradation of imazalil, the ratio of [alcohol]/[imazalil] = 500 was sufficient to inhibit the majority of hydroxyl radicals [26]. Here a ratio of [K₂S₂O₈]/[imazalil] = 100 was selected to avoid as much as possible interference between *tert*-butanol and SO₄•⁻. To resume, the ratio for [alcohol]/[K₂S₂O₈]/[imazalil] is 500/100/1.

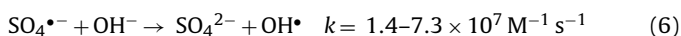
Table 2

Influence of the presence of *tert*-butanol (4.44×10^{-2} M) on the degradation of imazalil at different pH, $[K_2S_2O_8] = 8.88 \times 10^{-3}$ M, $[TiO_2] = 2.5$ g L $^{-1}$, $[imazalil] = 25$ mg L $^{-1}$.

Experiments	k (min $^{-1}$) (without <i>tert</i> -butanol)	k (min $^{-1}$) (with <i>tert</i> -butanol)	Inhibition (%)
UV–TiO $_2$ – pH 3	0.070	0.024	65.2
UV–TiO $_2$ – pH 6.5	0.111	0.036	67.6
UV–TiO $_2$ – pH 10	0.134	0.043	67.7
UV–K $_2$ S $_2$ O $_8$ – pH 3	0.150	0.149	0.4
UV–K $_2$ S $_2$ O $_8$ – pH 6.5	0.151	0.147	3.1
UV–K $_2$ S $_2$ O $_8$ – pH 10	0.150	0.142	5.4
UV–TiO $_2$ –K $_2$ S $_2$ O $_8$ – pH 3	0.466	0.434	6.9
UV–TiO $_2$ –K $_2$ S $_2$ O $_8$ – pH 6.5	0.278	0.186	33.2
UV–TiO $_2$ –K $_2$ S $_2$ O $_8$ – pH 10	0.127	0.061	51.5

Table 2 shows the rate constant values obtained with and without *tert*-butanol and the percentage of inhibition between them. In the system UV/TiO $_2$, an inhibition of about 66% was observed for the pH tested (3, 6.5 and 10) which confirms the results obtained in our previous work [26] showing that OH \cdot was mainly responsible for the degradation of imazalil.

In the UV/K $_2$ S $_2$ O $_8$ system, it is shown that *tert*-butanol does not affect significantly the degradation of imazalil, since similar rate constant values are obtained with and without scavenger. At acidic pH, no inhibition was observed whereas the percent of the inhibition increases to a maximum of 5% at pH = 10 due to the scavenging of little amount of hydroxyl radicals that could be formed according to Eq. (6)



We can conclude that the reaction between the sulfate radical and the *tert*-butanol does not occur in our working conditions and that reaction of sulfate radicals with imazalil is very efficient.

In the UV/TiO $_2$ /K $_2$ S $_2$ O $_8$ system, a difference in the percent of inhibition was observed as a function of the different pH. At pH = 3, a weak influence of *tert*-butanol was shown which could be attributed to a higher concentration of sulfate radicals versus OH \cdot (only 7% of inhibition), while an increase of the pH leads to an increase of the inhibition rate due to a higher production of OH \cdot .

These results confirm that (i) at acidic pH, S $_2$ O $_8^{2-}$ is well adsorbed on the TiO $_2$ surface and that SO $_4^{\bullet-}$ radicals formed are responsible for the degradation of imazalil (ii) at neutral pH both sulfate and hydroxyl radicals can participate to degrade the pollutant and (iii) at alkaline pH, hydroxyl radicals become more important (51.5%).

3.5. Comparison of imazalil photoproducts in the systems UV/TiO $_2$, UV/TiO $_2$ /K $_2$ S $_2$ O $_8$ and UV/K $_2$ S $_2$ O $_8$

Since we have shown that according to the system chosen and the experimental conditions, different kinds of radicals were formed, we can expect to obtain different mechanism of degradation. In this context, experiments were conducted at pH = 6.5 and with a ratio $[K_2S_2O_8]/[imazalil] = 100$. This ratio was chosen so that the reaction does not occur too quickly and that the kinetics of photoproducts can be easily followed. First it should be mentioned again that sulfate radicals could react with three different ways: hydrogen abstraction, addition on the double bond and by electron transfer. This latter is easily performed by sulfate radicals. The results have shown that the same photoproducts were obtained in the three systems but their evolutions during time were different. For example, hydroxyl photoproducts amount (mainly $m/z = 313$, see structure, Fig. 3) were less important in both systems using persulfate ions, leading to the idea that another mechanism other than hydroxylation is responsible of the degradation.

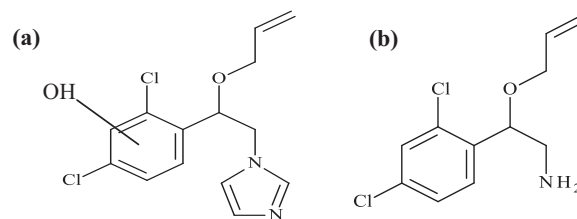


Fig. 3. Structure of photoproducts having m/z 313 (a) and 246 (b).

On the other hand, another remarkable conclusion is that the photoproduct having m/z 246 (Fig. 3, see structure) proposed coming from an electron transfer in our previous work [26] is mainly formed in systems containing persulfate ions. This photoproduct appears from the first minute and in a high amount. Its formation could be attributed to an electron transfer induced by sulfate radicals which does not occur on the benzene ring because of the presence of chlorines atoms which are electron acceptor but rather on the imidazole part containing nitrogen atoms. It is also noteworthy that the quantity of photoproducts in the system containing persulfate is very low, compared to UV/TiO $_2$ system which could be attributed to a more rapid mineralization.

3.6. TOC analyses at neutral pH

In the previous paragraphs, it has been shown that systems containing persulfate ions were more efficient than UV/TiO $_2$ system in terms of degradation of imazalil. However, the aim of any degradation is not only the degradation of the initial pollutant but also to achieve total mineralization. In this context, TOC analyses were conducted in the three systems. Experiments were performed at several interval times, going up to 4 h as maximum in the following conditions (pH = 6.5 and $[K_2S_2O_8]/[imazalil] = 250$). Fig. 4 shows that in the UV/K $_2$ S $_2$ O $_8$ system 2 h were sufficient to reach the total mineralization whereas more than 4 h were required in the UV/TiO $_2$ /K $_2$ S $_2$ O $_8$ system and more than 25 h for the UV/TiO $_2$ system [26]. These results confirm the efficiency of sulfate radicals to degrade and mineralize imazalil which is in agreement with other studies of other molecules [9,17,18,32–37]. However, it should be noted that if during the first hour of the degradation, the mineralization is faster in the UV/TiO $_2$ /K $_2$ S $_2$ O $_8$ system than in the UV/K $_2$ S $_2$ O $_8$ an inversion occurs beyond this time. This result could be explained by the adsorption of sulfate anions (produced according to Eq. (1)) onto TiO $_2$ surface which are going to reduce the adsorption of pollutants and/or persulfate ions [37,38].

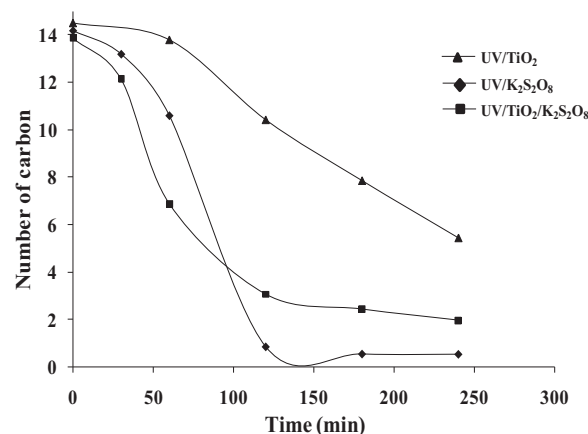


Fig. 4. TOC analysis for the three systems of degradation.

4. Conclusions

The study of degradation of imazalil in three different systems UV/TiO₂, UV/K₂S₂O₈ and UV/TiO₂/K₂S₂O₈ pointed to the beneficial effect of using persulfate during the degradation.

In the UV/TiO₂/K₂S₂O₈, the degradation was the fastest at pH = 3 due to a higher adsorption of persulfate anions onto TiO₂ surface and their reaction with electrons in the conduction band leading to the formation of more sulfate radicals.

In the UV/K₂S₂O₈, the pH does not play an important role in the degradation; the persulfate concentration is the determining factor.

As for experiments with *tert*-butanol, it has certified that whatever the pH, the sulfate radicals are major in the UV/K₂S₂O₈ system, as in the UV/TiO₂ system, hydroxyl radicals are responsible of about 66% of imazalil degradation while in the UV/TiO₂/K₂S₂O₈, the pH plays the major role in determining dominant radicals in the solution.

Furthermore, the comparison of photoproducts showed that (i) the quantity of photoproducts in systems containing persulfate are low comparing to UV/TiO₂, (ii) more hydroxylated products are presented in the UV/TiO₂ system and (iii) the photoproduct with *m/z* = 246 formed mostly by electron transfer is remarkably present in the systems containing persulfate.

In addition, TOC analysis at pH = 6.5 and [K₂S₂O₈]/[imazalil] = 250 has affirmed that the presence of persulfate improve the mineralization and the efficiency of the process was ranked in the following order: UV/K₂S₂O₈ > UV/TiO₂/K₂S₂O₈ > UV/TiO₂.

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